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ESTIMATION OF (Δr_e) OF AN ELECTRONIC BAND SYSTEM—A NEW METHOD

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ABSTRACT A new method of constructing the Morse potentials associated with an electronic band system without the knowledge of internuclear distances and estimating therefrom the difference (Δr_e) in the equilibrium distances in the two states has been suggested. The knowledge of this latter quantity (Δr_e) is an essential parameter in the theories of vibrational transition probabilities in molecular spectra.

1

Morse potential becomes defined when equilibrium internuclear distances are known But there are a number of band systems for which r_e values are not known, because of the difficulties of analysing the rotational structures. As such distances, or at least the difference between them for a transition, are essential for the problems of vibrational transition probabilities in electronic band spectra of diatomic molecules, it was thought worthwhile to explore the possibility of an indirect method, independent of rotational structure analysis to get a clue to the nearest, if not the precise estimate of the difference in internuclear equilibrium distances. The method and procedures are outlined in the following sections.

2

The usual Morse expression for potential energy

$$U = D_e(1-e^{-a\xi})^2 \qquad \ldots \quad (1)$$

can be converted to a slightly modified form

$$\frac{1}{a}\log_e\left(1+\sqrt{\frac{u}{D_e}}\right) = (r-r_e) \qquad \ldots \quad (2)$$

For $r_e = 0$, the Eq. (2) above becomes

$$\frac{1}{a}\log_e\left(1+\sqrt{\frac{u}{D_e}}\right) = -r \qquad \ldots \quad (3)$$

If a, u and D_e are assumed known, then the left hand side of Eqns. (2) or (3) above can be evaluated. These quantities are expressed as

$$a = 02454\sqrt{\mu\omega_e x_e}$$

$$U(= E_v) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2$$

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

Of these the quantity E_v is calculated for different values of v, i.e. 0, 1, 2, 3... and substituted in Eq. (2). We then get from it a set of values of $(r_e - r)$ corresponding to E_0, E_1, E_2, E_3... etc. which we could designate as r_0, r_1, r_2, r_3, ... etc. These are taken as one set of values about the equilibrium distance and are used for plotting the relevant part of the potential energy curve. It is then necessary to obtain points for other extremities of the vibrational levels for plotting the complementary part of the curve. This means another set of r values corresponding to E_0, E_1, E_2 and so on. For this purpose, since we are concerned with a harmonic oscillator the expression of Pillow (1951) can be made use of. According to Pillow, the centres of vibrational energy levels of an anharmonic oscillator lie at a distance of $(v+1)(x/a)$ from centres of the vibrational energy levels of the harmonic oscillator. Using this expression, the other set of r values will become

$$r_0+2(v_0+1)\frac{x}{a}$$

$$r_1+2(v_1+1)\frac{x}{a}$$

$$r_2+2(v_2+1)\frac{x}{a}$$

..... etc

The method of arriving at the above type of expressions is indicated below.

The vertical axis is at a distance of r_0 (for $v = 0$ level) from the point of intersection of the potential energy curve and the vibrational energy level. As the centre of the vibrational energy level of the anharmonic oscillator lies at a distance $(v_0+1)\frac{x}{a}$ from the vertical axis, the centre of the vibrational energy level of the anharmonic oscillator is at the distance $r_0+(v_0+1)\frac{x}{a}$ from the same point of intersection. So the distance from the vertical axis up to the point of intersection to the right will be

$$r_0+(v_0+1)\frac{x}{a}+(v_0+1)\frac{x}{a}$$

or,

$$r_0+2(v_0+1)\frac{x}{a}$$

Now starting with $r_e = 0$, which may be taken as the origin and making use of these two sets of r-values and the vibrational energy E_v, the potential energy curves both for the upper and lower states of transition can be drawn. Some of these r-values for the $A^3\pi$ state of the C_2 molecule have been derived and shown in Table I.

TABLE I

Derived r-values for C_2, $A^3\pi$ state.

v	$(v+1)x/a$ A.u	$E_v(cm^{-1})$	$(-)$Å	$(+r)$ i.e. $r+2(v+1)(x/a)$Å
0	0.003784	889 9	0 05206	0.05963
1	0 00757	2645.3	0 08596	0 10109
2	0 01135	4367 8	0.1074	0.1301
3	0.01514	6057 3	0.1241	0.15438
4	0 01862	7713 9	0 1374	0.17464
10	0.04162	16963 5	0.1902	0.27344

The assumption made above about the origin, i.e. $r = 0$ means that the two curves for the pair of the states involved are drawn about a common vertical axis. This is not enough as the curves need to be disposed with respect to the position of the minimum as well as with respect to their energy difference, i.e. the horizontal shift as well as the vertical shift. The steps for obtaining these relative dispositions are indicated below.

It is an established fact that if $\omega_e' > \omega_e''$ then $r_e' < r_e''$ and vice versa. So from the ω_e values, we know the direction in which the curve for the upper state is to be shifted with respect to the lower curve on the horizontal axis.

If the intensities of the bands are known fairly accurately or could be estimated, then it is possible to fix the Condon parabola or the most probable transitions. By trial the curve is shifted in the proper direction along horizontal axis until the most probable transitions known as above, are reached. When this is achieved carefully, one could get the nearest approximation to the quantity (Δr_e).

To test the performance of the method outlined above, some well-established band systems were selected for study. Experimental intensity data as well as r_e—values in both the states are accurately known for these systems. One could construct the potential energy curves and derive the (Δr_e) value in the manner shown above. On the other hand, there is the knowledge of the exact value of this quantity from the rotational structure analysis constants. Both these values for the band systems chosen are recorded in Table II. How far the estimated values depart from exact experimental data is shown by calculating the percentage departure.

TABLE II

Comparative study

Molecule	Transition	Δr_e Å		Percentage departure from expl. value
		Present	Expl. value (Herzberg, 1950)	
C_2(Swan)	$A\,^3\pi - X^3\pi$	0.04	0.046	−13.0
AlO	$A\,^2\Sigma - X^2\Sigma$	0.045	0 049	− 8.2
BO-α	$A\,^2\pi - X^2\Sigma$	0.160	0.1475	+ 8.8
BO-β	$B\,^2\Sigma - X^2\Sigma$	0.095	0 1061	−10.4
CN-violet	$B\,^2\Sigma' - X^2\Sigma'$	0.0225	0.0212	+ 6 1
N_2(IIP)	$C\,^3\pi - B^3\pi$	0.055	0 0641	−14 2
MgO	$B\,^1\Sigma - X^1\Sigma$	0 011	0.012	− 8 3

For certain band systems, estimates have been made by earlier workers on the basis of empirical relations or other methods We can pick up one of these systems to see how far the forecast of (Δr_e) from the present method stands in relation to other estimates The system to which we would refer is the ($C-B$) transition of *BO*. Katti (1957) by applying 4 different methods or rules has estimated the Δr_e−difference for this system. These estimates are recorded in Table III in which also, is included the value predicted from the present method

TABLE III

Relation or method used	Δr_e-estimates	Å
Morse (1929)	0 1204	Katti (1957)
Birge (1932) and Mecke (1925)	0.1035	,,
Wu and Chao (1947)	0.0720	,,
Nicholls (1955)	0 1503	,,
Present method	0.095	

It is evident from the results of Table III that the value derived from the method suggested here compares favourably with the data derived from other methods and particularly Birge and Mecke's relation. Although Katti is inclined to favour the value from Morse's relation, the approach made by the present method is the next best like Birge and Mecke's among the few methods or relations that are available. The true situation with regard to any of these methods will not be gauged unless we have in our possession the measured r_e-values from rotational structure analysis.

The advantage of the method is that it is entirely independent of any of the two r_e-values of the electronic states involved and requires the parameters, viz., ω_e and $\omega_e x_e$ which are generally provided by vibrational analysis and the knowledge of the most probable transitions from vibrational intensity data.

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